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Reaction of $[\text{AuCl}_3(\text{CNR}^1)]$ ($\text{R}^1 = \text{Xyl, Cy, (S)-CHMePh}$) with amines unexpectedly proceeds *via* the redox pathway giving gold(i)-isocyanides and imines, while the addition of benzophenone hydrazone to the isocyanide ligand in $[\text{AuCl}_3(\text{CNR}^1)]$ at RT leads to short-lived gold(iii) acyclic diaminocarbene complexes $[\text{AuCl}_3(\text{C}(\text{NHNCPh}_2)\text{NHR}^1)]$.

In recent years, complexes with N-heterocyclic carbenes (NHCs) and acyclic diaminocarbenes (ADCs) have emerged as valuable alternatives to other traditional catalysts in a number of organic transformations.¹ Most common routes to their preparation include (i) a coordination of the pre-formed carbenes (generated *in situ* from appropriate precursors and a base, or obtained *via* transmetalation from M-NHCs) to a metal center,^{1b,e,2} (ii) an oxidative addition of appropriate carbene precursors to electron-rich metal centers,^{1d,e,2} and (iii) a metal-mediated nucleophilic addition or a dipolar cycloaddition to isocyanides.^{1a,2,3}

A few reported Au(iii)-NHC complexes were generated *via* (i) oxidation of the corresponding Au(i)-NHC species using X_2 ($\text{X} = \text{Cl, }^4 \text{Br, }^{4b,5} \text{I}^{4b,5a,6}$), PhICl_2 ,^{4a,5,6b,7} ICl ,^{5b,6b} ICF_3 ,^{5b} or CsBr_3 ,⁸ (ii) reaction of *N*-alkyltriazolium salts with $\text{H}[\text{AuCl}_4]$ ⁹ or $\text{Na}[\text{AuCl}_4]$ ¹⁰ followed by addition of a base, or interaction of lithiated triazole with $[\text{AuCl}_3(\text{THT})]$ (THT = tetrahydrothiophene) followed by addition of an acid;¹¹ (iii) treatment of $\text{Na}[\text{AuCl}_4]$ with $\text{C}\equiv\text{N}(\text{CH}_2)_n\text{OH}$ leading to a substitution of chloride with the isocyanide with consecutive intramolecular attack of the OH group on the carbon of the coordinated isocyanide;¹² (iv) transmetalation of the carbene ligand from the Ag(i), W(i), or Cr(i) to Au(iii) center;¹³ and (v) disproportionation of Au(i)-NHC in the presence of $[\text{AuCl}(\text{SMe}_2)]$ furnishing Au(iii)-NHC complexes and metallic gold.¹⁴

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Addition of *N*-nucleophiles to gold(iii)-bound isocyanides leading to short-lived gold(iii) acyclic diaminocarbene complexes†

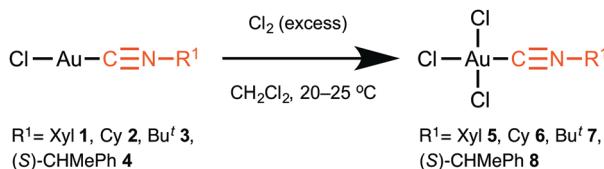
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As far as open-chain acyclic diaminocarbenes bound to a gold(iii) center are concerned, data available are even more scarce than those for gold(iii)-NHC congeners and only a few gold(iii)-ADCs were reported. The known gold(iii)-ADCs are mostly derived from the oxidative addition of bromine and iodine to the corresponding gold(i)-ADCs.¹⁵ Single examples of other approaches include (i) intramolecular attack of the cycloaurated 2-(2-pyridylamino)phenyl ligand on an isocyanide;¹⁶ carbene transmetalation from the chromium(i) to the gold(iii) center;¹⁷ and (ii) amine addition to gold(iii)-bound CNRs.¹⁸

Although the complexes of gold(i) with ADC ligands^{1a,15b,19} are commonly assembled *via* the addition of $\text{sp}^3\text{-N}$ and $\text{sp}^3\text{-O}$ nucleophiles to gold(i)-isocyanides, only two examples of nucleophilic addition to gold(iii)-CNRs were reported. Thus, Bartel and Fehlhammer studied¹² the reaction of $\text{Na}[\text{AuCl}_4]$ with $\text{C}\equiv\text{N}(\text{CH}_2)_n\text{OH}$ leading to the substitution of a chloride with the isocyanide followed by an intramolecular attack of the OH group on the C-atom of the coordinated isocyanide¹² giving an NHC-Au(iii) complex; the intermediate ADC species were not isolated but postulated as reaction intermediates. In the other study, addition of amines to the isocyanide in $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{p-CNC}_6\text{H}_4\text{Me})]$ gave the corresponding gold(iii)-ADC species,¹⁸ no spectroscopic properties of these complexes were observed.¹⁸ Intrigued by a limited number of known gold(iii)-ADCs, we aimed to expand their family *via* the reaction of other gold(iii)-isocyanide precursors, *viz.* $[\text{AuCl}_3(\text{CNR}^1)]$, with different NH-nucleophiles. Considering limited spectroscopic data reported for a few known gold(iii)-ADCs, we also aimed to extensively characterize new gold(iii)-ADC species.

We initiated this study from the preparation of gold(iii)-isocyanides *via* the oxidative addition of chlorine to $[\text{AuCl}(\text{CNR}^1)]$ (Scheme 1). Thus, vigorous bubbling of dry gaseous chlorine through a solution of $[\text{AuCl}(\text{CNR}^1)]$ ($\text{R}^1 = \text{Xyl } \mathbf{1}; \text{Cy } \mathbf{2}, \text{Bu}^t \mathbf{3}, (\text{S})\text{-CHMePh } \mathbf{4}$) in dry CH_2Cl_2 led to the formation of the corresponding complexes $[\text{AuCl}_3(\text{CNR}^1)]$ ($\text{R}^1 = \text{Xyl } \mathbf{5}; \text{Cy } \mathbf{6}, \text{Bu}^t \mathbf{7}, (\text{S})\text{-CHMePh } \mathbf{8}$). At 20–25 °C, all reactions were completed almost immediately furnishing gold(iii)-isocyanide species that were isolated as either yellow crystalline solids (**5–7**) or an yellow oily residue (**8**) in 96–99% yield. Preparation of the related



Scheme 1 Chlorination of **1–4** leading to gold(III)-isocyanides.

[AuBr₃(CNR¹)] species *via* the oxidative addition of bromide to [AuBr(CNR¹)] was previously described.²⁰

The prepared isocyanide complexes **5–8** were characterized by ESI^{+/−}-MS, FT-IR, ¹H and ¹³C/¹H NMR spectroscopy, while complexes **6** and **7** were characterized additionally by CHN elemental analyses, and **5** by single-crystal X-ray diffraction (Fig. 1S and 2S in the ESI[†]).

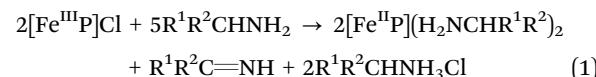
Amines are sp³-N nucleophiles conventionally used for coupling with coordinated isocyanides, including gold(I)-CNRs,^{1a} therefore, we have selected representative primary and secondary amines as our first choice in the reaction with gold(III)-isocyanides.

Reaction of [AuCl₃(CNR¹)] with amines. Reaction of complexes **5–8** with one or two equivalents of primary (benzylamine **9**) or secondary (morpholine **10**) amine in CH₂Cl₂ led to the formation of the corresponding amine hydrochloride and the product of reduction of the starting complex in solution (to **1–4**, respectively) along with some yet unidentified species. With the more sterically hindered α -methylbenzylamine (**11**) as a nucleophile, the reaction proceeds *via* an unusual reduction pathway (Scheme 2).

Thus, the reaction of equimolar amounts of any one of **5–8** with **11** in CH₂Cl₂ at −74 °C led to the precipitation of complex salt **12** as a bright yellow crystalline solid (*ca.* 20% yield). The maximum yield of **12** (40–42%) was achieved with a **5–8** to **11** ratio of 2:3. In the solution, the presence of **12**-HCl and respective gold(I)-isocyanide complexes **1–4**, alongside 1-phenylethan-1-imine and trace amounts of some yet unidentified species, was established using ESI-MS, FT-IR, and ¹H NMR spectroscopy. No carbene complexes were detected in this mixture. Similar results were obtained for optically pure α -(*R*)-methylbenzylamine (**R**)-**11**. Complex salts **12** and (**R**)-**12** were isolated and characterized by elemental analyses, ESI-MS, FT-IR and NMR and X-ray diffraction for (**R**)-**12** (see the ESI[†]).

We attempted to shed light on the nature of this process. In the early works by Castro *et al.*,²¹ oxidation of the amines by

iron(III)-porphyrins led to the formation of appropriate imines as oxidation products, corresponding iron(II)-porphyrine complexes as reduction products as well as amine hydrochlorides (eqn (1)). Reduction of gold(III)-NHCs to the corresponding gold(I)-derivatives in the presence of free isocyanide is also known from the studies of Bartel and Fehlhammer.¹²

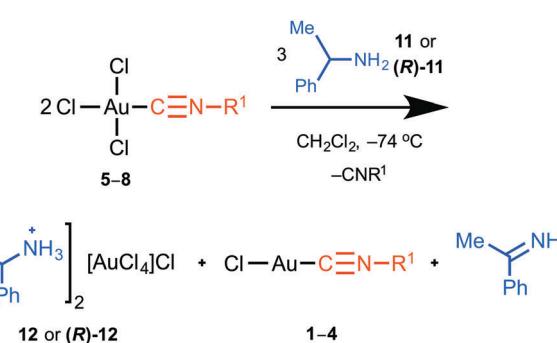


Taking these data into consideration and on the basis of our experimental evidence (gold(I)-isocyanides **1–4**, free isocyanide and 1-phenylethan-1-imine were identified in the reaction mixture) as well as the observed stoichiometry, we assume that the overall reaction of **5–8** with **11** proceeds *via* the redox pathway depicted in Scheme 2. Herein, one equiv. of methylbenzylamine (**11**) is oxidized to 1-phenylethan-1-imine by one equiv. of gold(III)-isocyanides (**5–8**) that are simultaneously reduced to the corresponding gold(I) species (**1–4**). Two equivalents of protons that are released during this oxidation are accepted by two additional equivalents of free amine furnishing the corresponding quaternary ammonium salt [Ph(Me)CHNH₃]⁺Cl[−]. This further reacts with the second equiv. of [AuCl₃(CNR¹)] giving rise to a complex salt **12** and free isocyanide. To the best of our knowledge, this gold(III)-mediated oxidation of amines was not previously reported. In the earlier study, addition of amines to [Au(C₆F₅)₃(*p*-CNC₆H₄Me)] gave the corresponding gold(III)-ADC species, and no oxidation of amine by gold(III) was observed.¹⁸ We believe that this can be rationalized by a stronger sigma donation from the coordinated C₆F₅ in [Au(C₆F₅)₃(*p*-CNC₆H₄Me)] (when compared to that from chlorides in **5–8**) resulting in a decrease of the oxidation potential of gold(III) below the required threshold.

Insofar as our attempts to prepare gold(III)-ADCs *via* coupling of gold(III)-CNRs with amines led to the oxidation of the latter, we focused our attention on hydrazines that are stronger nucleophiles than the relevant amines due to the α -effect.²² Among hydrazine derivatives, aldo- and ketohydrazones are recognized as the most stable toward oxidation²³ and were selected for further studies.

Reaction of [AuCl₃(CNR¹)] with hydrazones. Recently we reported the addition of aldo- and ketohydrazones to an isocyanide ligand in *cis*-[MCl₂(CNR)₂] (M = Pd(II), Pt(II)) that result in the corresponding aminocarbene species.²⁴ Extensive experimental and theoretical studies on the properties of hydrazones²⁵ revealed that the hybridization of the NH₂ center is intermediate between sp³-N and sp²-N, and it depends strongly on the nature of substituents, approaching sometimes the pure sp²-N state.

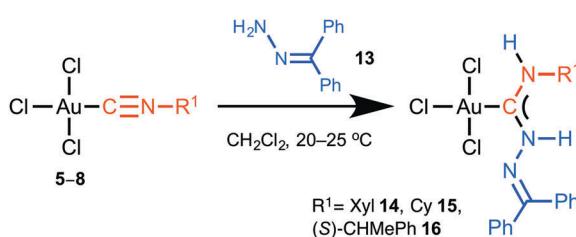
To our knowledge, nucleophilic attack of H₂N-N=CPh₂ on gold-bound isocyanides has never been described, presumably because Au(I) does not provide sufficient electrophilic activation to a coordinated isocyanide moiety toward nucleophilic attack. To compare the susceptibility of gold(III)- and gold(I)-isocyanides toward nucleophilic attack, we carried out theoretical DFT calculations [*viz.*, a geometry optimization procedure in the gas phase, calculations of vibrational frequencies, and

Scheme 2 Interplay between α -methylbenzylamine and Au^{III}-isocyanide complexes.

natural bond orbital (NBO) analysis] using $[\text{AuCl}_3(\text{CNMe})]$ and $[\text{AuCl}(\text{CNMe})]$ as model compounds (see full details in the ESI[†]). The energy level of the first unoccupied MO bearing $\pi^*(\text{C}\equiv\text{N})$ orbitals (*viz.*, LUMO-1, Fig. S3, ESI[†]) in $[\text{AuCl}_3(\text{CNMe})]$ (-2.07 eV) is significantly lower than that in $[\text{AuCl}(\text{CNMe})]$ (-1.47 eV), suggesting that the Au(III) center is a stronger activator of the isocyanide ligands toward the addition of nucleophiles. The computed NBO charges on isocyanide carbon atoms in $[\text{AuCl}_3(\text{CNMe})]$ and $[\text{AuCl}(\text{CNMe})]$ are 0.44 and 0.30, respectively. Finally, the calculated value of the unscaled normal mode frequency $\nu(\text{C}\equiv\text{N})$ in $[\text{AuCl}_3(\text{CNMe})]$ (2389 cm^{-1}) is greater than that in $[\text{AuCl}(\text{CNMe})]$ (2321 cm^{-1}), and this reflects higher electrophilic activation of CNRs bound to the gold(III) center.^{3a} Note that these calculated values of the normal mode frequencies $\nu(\text{C}\equiv\text{N})$ are unscaled, and are expectedly overestimated.²⁶ Recommended multiplication of the calculated $\nu(\text{C}\equiv\text{N})$ values on the scaling factor 0.96 gives 2293 cm^{-1} and 2228 cm^{-1} , respectively, and it is in perfect agreement with the experimental data.²⁶ Thus, orbital, charge, and frequency arguments reveal that the Au(III) center is a better activator of the CNR ligand toward nucleophilic addition when compared to Au(I). Taking these results into consideration, we studied the reactivity of Au(III)-isocyanide complexes in the coupling with hydrazones.

Reaction of 5, 6, or 8 with benzophenone hydrazone (13, 1 equiv.) in dry CH_2Cl_2 proceeds at RT for *ca.* 15 min giving the short-lived complexes $[\text{AuCl}_3\{\text{C}(\text{NHNCPh}_2)\text{NHR}^1\}]$ ($\text{R}^1 = \text{Xyl}$ 14; Cy 15, (*S*)-CHMePh 16; Scheme 3). No such reaction was observed between 7 and 13, which is apparently because of the low reactive Bu^tNC .²⁷ Reaction of 5-8 with 9-fluorenone hydrazone (17) and salicylaldehyde hydrazone (18) in dry CH_2Cl_2 or toluene at RT led to the formation of unstable species that almost immediately decompose giving metallic gold and a solution of yet unidentified species.

Compounds 14 and 16 possess low stability in solution and in the solid state, but we could characterize them by FT-IR, ESI-MS, and ^1H and $^{13}\text{C}\{^1\text{H}\}$ (only for 14) NMR spectroscopy. In addition, the structure of 14, which was stable enough at 150 K when compared to those of 15 and 16, was elucidated by single-crystal X-ray diffraction. Compound 15 rapidly (*ca.* 10 min) decomposes both in solution and in the solid state, and was characterized solely by solution ^1H NMR spectroscopy immediately after its formation. The detailed characterization of 14-16 is provided in the ESI,[†] and herein we discuss the most important details of the solid-state X-ray structure of complex 14 (Table S1, the ESI[†] contains crystallographic data and processing parameters for 14).



Scheme 3 Nucleophilic addition of benzophenone hydrazone to Au^{III}-bound isocyanide.

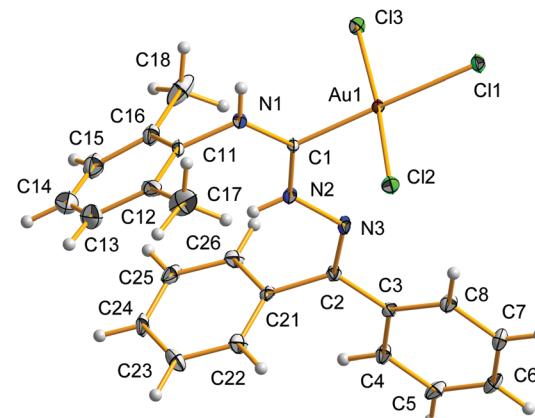


Fig. 1 Crystal structure of 14 with the atomic numbering scheme (hydrogen labels and chloroform molecules were omitted for simplicity). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (\AA) and angles ($^\circ$): Au1–Cl1 2.3255(12), Au1–Cl2 2.2687(14), Au1–Cl3 2.3001(14), Au1–C1 2.005(5), C1–N1 1.312(6), C1–N2 1.318(5), C2–N3 1.293(6), N2–N3 1.387(5), C1–Au1–Cl1 178.55(12), C1–Au1–Cl2 87.21(16), C1–Au1–Cl3 89.29(16), Cl1–Au1–Cl2 92.63(5), Cl2–Au1–Cl3 175.16(5), N1–C1–Au1 121.9(3), N1–C1–N2 118.4(4), N2–C1–Au1 119.7(3).

The asymmetric unit of 14 contains one molecule of the complex and one of chloroform (Fig. 1). The square-planar coordination environment of 14 ($\tau_4 = 0.05$)²⁸ is filled by one carbene and three chloride ligands. All bond angles around the Au(III) center are close to 90° varying from $87.21(16)^\circ$ to $92.63(5)^\circ$. The Au–Cl1 ($2.3255(12)$ \AA) distance opposite to the carbene fragment is slightly longer than the other two Au–Cl distances ($2.2687(14)$ and $2.3001(14)$ \AA) and that in 5 ($2.2687(19)$ \AA) indicating significant ground-state *trans* influence of the carbene ligand when compared to the parent isocyanide in 5. The Au–C bond distance ($2.005(6)$ \AA) is comparable to those observed in 5 ($1.954(7)$ \AA) and in the related complexes containing N-heterocyclic carbenes $[\text{AuCl}_3(\text{IMes})]$ ($2.016(7)$ \AA),⁹ $[\text{AuCl}_3(1,3\text{-dihydro-1-methyl-3-(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene}]]$ ($1.994(4)$ \AA),⁷ and $[\text{AuCl}_3(\text{IPr})]$ ($2.013(9)$ \AA).^{4a} The carbene moiety is almost planar (C1 deviates from the Au1–N1–N2 plane by 0.017 \AA) and the angles around the carbene C1 atom are nearly equal to 120° varying from $118.4(4)^\circ$ to $121.9(3)^\circ$, indicating its sp^2 hybridization. Both C_{carbene}–N distances are equal within 3σ ($1.312(6)$ and $1.318(5)$ \AA) and their values are typical for delocalized one-and-a-half C–N bond (*e.g.* $1.337(12)$ for C_{ar}–N in pyridine).²⁹ The carbene plane (built on N1, C1, and N2 atoms) is almost perpendicular to the plane defined by the chloride ligands (angle of 77.66°). The carbene C1–N1 and C1–N2 bonds adopt *E*- and *Z*-configurations, respectively. The solid-state structure of 12 exhibits intermolecular T-shaped C–H \cdots π interactions involving both the C26–H8 and the C23–H10 bonds of every molecule and the C3–C8 phenyl rings of adjacent ones. Such interactions give rise to infinite chains along the crystallographic *a* axis (see the ESI[†] for more details).

Finally, evaluation of the bonding situation in the dimeric clusters of 5, 14, and (R)-12 was carried out using theoretical DFT calculations and topological analysis of the electron density distribution within the formalism of Bader's theory (QTAIM analysis);³⁰ this approach has already been successfully used by



us in the studies of non-covalent interactions and properties of coordination bonds in various transition metal complexes.³¹ QTAIM analysis (Table S2, ESI†) indicates the presence of two bond critical points (3, -1) (BCPs) for covalent bonds Au-Cl and two BCPs for Au···Cl non-covalent interactions, and no BCPs for Au···Au contacts in all studied dimers. The magnitudes of the electron density, values of the Laplacian and energy density, the $-G(\mathbf{r})/V(\mathbf{r})$ ratio in BCPs for Au-Cl and Au···Cl contacts as well as appropriate Wiberg bond indices (WI) are typical for covalent bonds M-L in coordination complexes and for non-covalent electrostatic interactions, respectively. We have defined energies for these contacts according to the procedures proposed by Espinosa *et al.*³² and Vener *et al.*³³ (Table S2, ESI†), and one can state that the relativistic and non-relativistic approaches give very similar estimates. The results of theoretical calculations led to the conclusion that weak Au···Cl non-covalent electrostatic interactions are most likely responsible for the stabilization of dimeric associates 5, 14, and (R)-12 in the solid state.

As a conclusion, direct oxidative addition of chlorine to [AuCl(CNR¹)] gives the corresponding Au^{III}-CNR species in nearly quantitative yields. Attempted nucleophilic addition of amines to gold(III)-isocyanides does not lead to carbene complexes but furnishes imines and gold(I)-isocyanides generated *via* the redox pathway. At the same time, addition of benzophenone hydrazone to the coordinated isocyanide in [AuCl₃(CNR¹)] furnishes new types of short-lived gold(III)-ADC species that gradually decompose to give metallic gold. Insofar as the stability of gold(III)-ADCs is concerned, one should consider that although the instability of complexes has a negative impact on their shelf-life, it might turn positive for their catalytic activity. It is argued that many modern organometallic catalytic processes, *i.e.* cross-coupling, are essentially catalysed by the nano-sized particles formed from the starting molecular compounds during the precatalyst activation step.³⁴ Herein, *in situ* prepared gold(III)-ADCs can promptly generate gold nanoparticles enabling subsequent catalytic transformations and further studies in this direction are currently underway in our group.

Acknowledgements

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